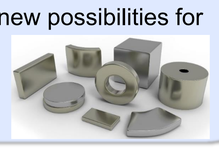
Pyrometallurgical Recovery of Rare Earth Elements from oxidized spent NdFeB-magnets via Carbothermic Reduction

Hanwen Chung[1], Buse Polat[1], Elif Emil Kaya [1,2,3], Srecko Stopic[1,*], Sebahattin Gürmen[2], and Bernd Friedrich [1]
[1]IME Process Metallurgy and Metal Recycling, RWTH Aachen University, 52056 Aachen, Germany; hanwen.chung@rwth-aachen.de
[2]Department of Metallurgical & Materials Eng., Istanbul Technical University, 34469 Istanbul, Turkey; gurmen@itu.edu.tr
[3]Department of Materials Science and Tech., Turkish-German University, 34820 Istanbul, Turkey; emil@tau.edu.tr

1. BACKGROUND, PREVIOUS WORK AND RESEARCH NEEDS FOR RECYCLING OF NdFeB-MAGNETS

Background

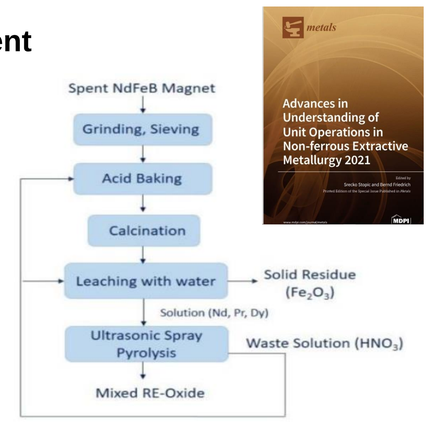
1. Rare Earth Elements REE (Lanthanoides) belong to critical metals in world industry
2. They have similar properties and it is difficult to separate
3. Most important minerals are bastnasite, monazite, xenotime, steenstrupine (radioactive) and eudialyte
4. The primary production is related to many different operations starting from grinding, flotation, Leaching, precipitation, solvent extraction and filtration
5. Recycling ("Urban Mining") offers new possibilities for REE-Recovery



Previous work: Hydrometallurgical treatment

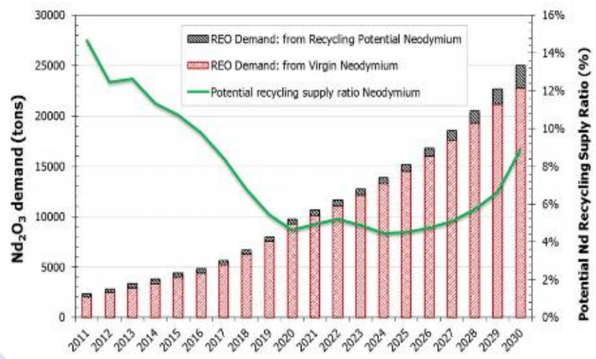
1. Leaching under atmospheric pressure
2. Leaching under high pressure in an autoclave
3. Backing process
4. Precipitation
5. Solvent extraction
6. Ultrasonic spray pyrolysis

Kaya, E., Kaya, O., Stopic, S., Gürmen, S., Friedrich, **NdFeB Magnets recycling process: An alternative method to produce mixed rare earth oxide from scrap NdFeB magnets**, *Metals* 2021, 11, 716,



Motivation (Research challenge)

1. Reduce import dependency
2. Recovery of secondary raw materials by means of recycling
3. End-of-Life Products vastly available
4. Separation of rare earths oxide and produced iron after carbothermal reduction



2. AIMS, PROPOSED METHOD AND MATERIAL

The problem in hydrometallurgy: Separation of Iron from the other elements is very difficult

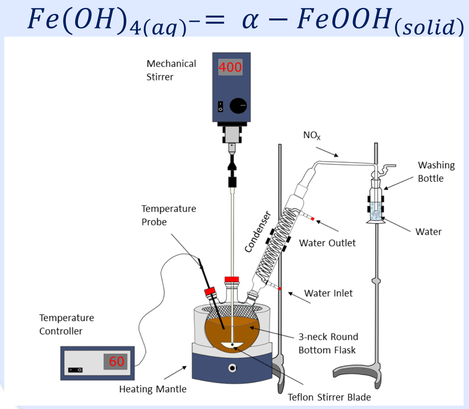
$$O_{2(g)} \leftrightarrow O_{2(aq)}$$

$$Fe^{3+} + H_2O = Fe(OH)_2 + H_2$$

$$Fe(OH)_2 + \frac{1}{4}O_2 + \frac{1}{2}H_2O = Fe(OH)_{3(solid)}$$

$$Fe(OH)_{3(solid)} + OH^- = Fe(OH)_{4(aq)}^-$$

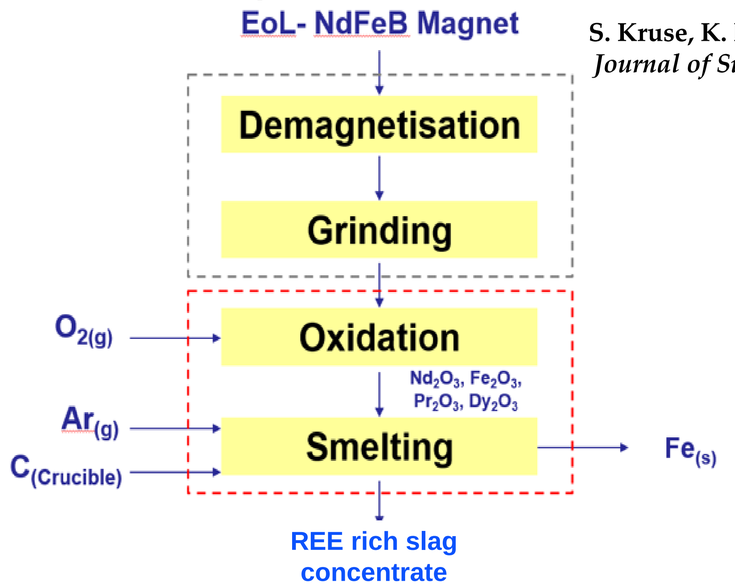
$$Fe(OH)_{4(aq)}^- = \alpha - FeOOH_{(solid)} + H_2O + OH^-$$



Main Aims

1. Recovery of rare earth elements from NdFeB-magnets by pyrometallurgical treatment
2. Production of concentrate bearing REEE, which is suitable for the pyrometallurgical and hydrometallurgical treatment
3. Separation of boron, nickel and iron from rare earth elements

Proposed Method for REE- Recovery



S. Kruse, K. Raulf, T. Pretz, B. Friedrich, *Journal of Sustainable Metallurgy*, 3, 1, 168–178, 2017

Material

EoL Magnet from Mıknatıs Ar-Ge

After demagnetising

Vibratory milll

After grinding

Samples in wt,%	Nd	Ni	Fe	B	Pr	Dy
NdFeB	15.9	0.0006	73.8	0.662	5.6	0.201
NdFeB+Ni	18.7	0.831	69.7	0.668	4.4	0.352

3. EXPERIMENTS AND RESULTS

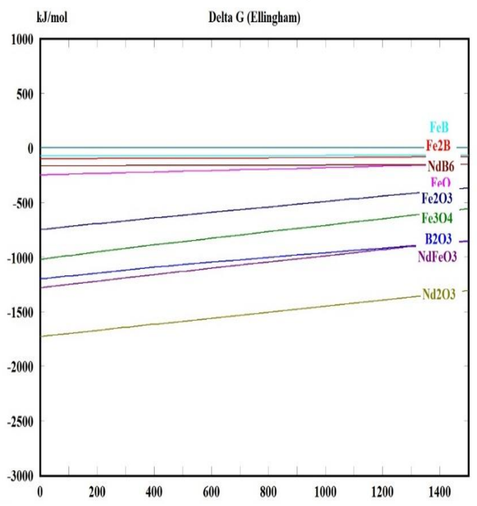
3.1. Oxidation

Mechanism of oxidation

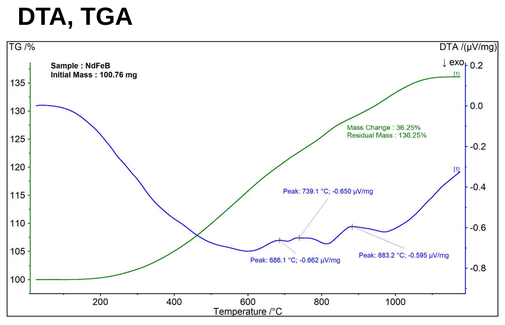
$Nd_2Fe_{14}B + 1.5\ O_2 = 2\ NdFeO_3 + 12\ Fe + 14\ B$
$4\ Nd_2Fe_{14}B + 45\ O_2 = 4\ Nd_2O_3 + 26\ Fe_2O_3 + 4\ FeB$

$Pr_2Fe_{14}B + 1.5\ O_2 = 2\ PrFeO_3 + 12\ Fe + 14\ B$
$4\ Pr_2Fe_{14}B + 45\ O_2 = 4\ Pr_2O_3 + 26\ Fe_2O_3 + 4\ FeB$

Thermochemical analysis

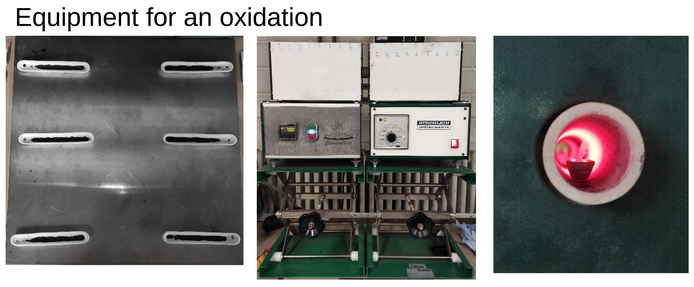


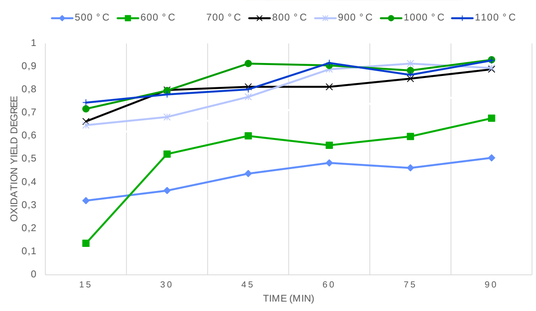
DTA, TGA



The oxidation in air confirmed that all elements are oxidized, and no selective oxidation according to thermochemical analysis.

Equipment for an oxidation



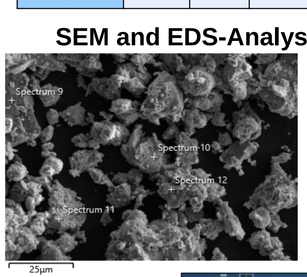


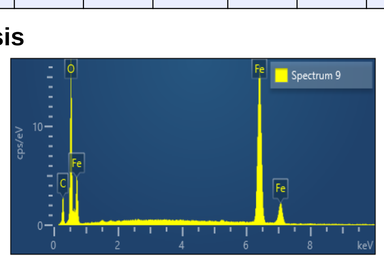
Maximal oxidation amounts 90 % at 900°C in 45 min (thereof 8 % for REE-oxidation)

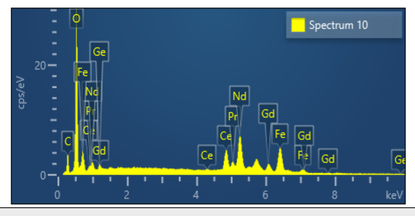
XRD-Analysis

Phase	Dy_2O_3	FeB_2	Fe_2O_3	Fe_3O_4	$NdBO_3$	$NdFeO_3$	Nd_2O_3	α-Fe	Pr_2O_3
Weight %	1.28	1.75	53.41	10.37	10.01	16.45	0.45	5.22	1.07

SEM and EDS-Analysis

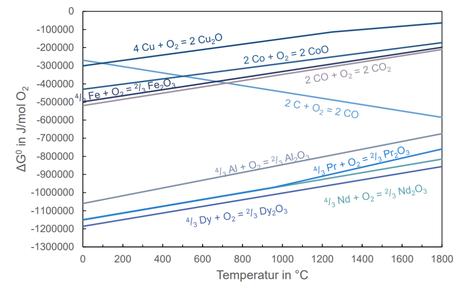






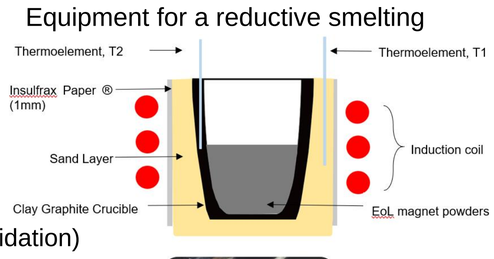
3.2. Reductive smelting of oxidized magnets in carbon crucible

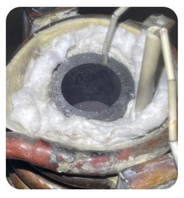
Richardson-Ellingham diagram for selected metals

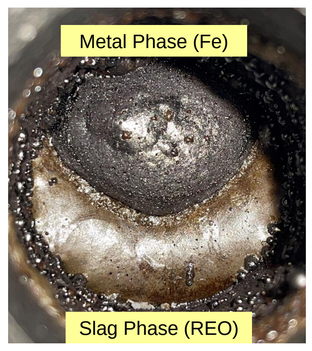


$3Fe_2O_{3\,(l)} + C_{(crucible)} \rightarrow 2\ Fe_3O_{4\,(l)} + CO_{(g)}$
$Fe_3O_{4\,(l)} + C_{(crucible)} \rightarrow 3\ FeO_{(l)} + CO_{(g)}$
$FeO_{(l)} + C_{(crucible)} \rightarrow Fe_{(l)} + CO_{(g)}$

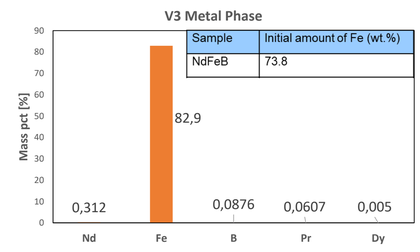
Equipment for a reductive smelting



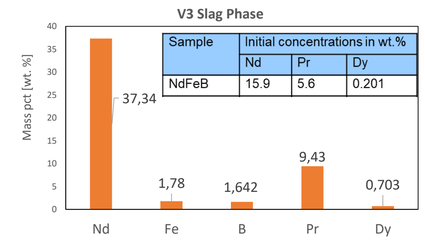




- Intensive convection
- Increased in furnace pressure
- Agglomeration & sintering of powder



Content of the V3 metallic phase



Content of the V3 Slag concentrate

Trials	Sample	Mass [g]	Temperature [°C]	Holding Time [min]
V1	NdFeB+Ni	100	1500	10
V2	NdFeB+Ni	60	1500	13
V3	NdFeB	57	1400	11
V4	NdFeB	60	1350	3

4. CONCLUSIONS

- At 1400 °C smelting temperature, metallic phase has 92.3 wt.% Fe and Slag phase showed a maximum total REE (Nd, Pr and Dy) content of 47.5 wt.%
- ICE-OES and XRD analysis were conducted on both phases, and results showed that the metal phase consists mainly of Fe and Fe_3C while the slag phase consists of the RE-oxides, leftover Fe_2O_3 and a mixture of Fe_6Nd_4.
- New concentrate of rare earth elements is formed after pyrometallurgical treatment confirming the strategy proposed by S. Kruse.

The next step is a treatment of REE-reach slag concentrate with molten salt electrolysis or by using an hydrometallurgical route

This research was funded by Federal Ministry for Economic Affairs and Climate Action, grant number 273 EN Project "Sustainable recovery of rare earth elements (Nd, Pr, Dy) from spent magnets".

Priv. Doz. Dr.-Ing. habil. Srecko Stopic
Tel.: + 49 241 80 95860
sstopic@ime-aachen.de